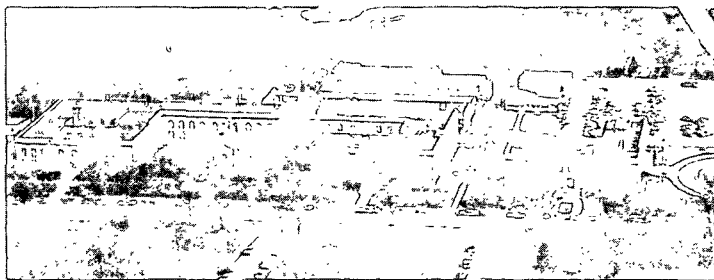


JAN 7 '76

MacMillan Div. Research Library  
LIBRARY TECHNICAL FILES



THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES

NUMBER 15

2

THE EFFECT OF OXYGEN CONSUMPTION DURING BLEACHING ON THE  
PROPERTIES OF A SOUTHERN PINE KRAFT PULP

N. S. THOMPSON AND H. M. CORBETT

SEPTEMBER, 1975

## INTRODUCTION

This report describes the initial investigations of oxygen-alkali delignification carried out at The Institute of Paper Chemistry. Although it was known that pulps could be bleached with oxygen, the limitations of the process were not fully understood. By recognizing the autoxidative character of the process and studying the process from a kinetic point of view, we were able to evaluate the significance of several process variables - alkalinity, oxygen pressure, transition metal ion content and pulp character - and point out potential difficulties unique to oxygen pulping.

MacMillan-Bloedel Research Limited  
LIBRARY TECHNICAL FILES

This paper is being submitted to Tappi for publication.

# The effect of oxygen consumption during bleaching on the properties of a southern pine kraft pulp

N. S. Thompson and H. M. Corbett

## Abstract

A commercial southern pine kraft pulp was used to study the effect of varying the concentration of oxygen, alkali and transition metal ions on certain pulp properties in order to evaluate the potential of oxygen delignification procedures. The results indicate that the degradation of the pulp is related to the amount of oxygen consumed during the reaction. In the presence of transition metal ions an increased influence of oxygen consumption on pulp degradation becomes apparent, which is directly related to the alkalinity of the system. It is suggested that cellulose degradation will be lessened when less oxygen is used for delignification or when the effect of the intermediate peroxide on the cellulose and fiber structure is minimized.

## INTRODUCTION

Many investigations have described the reaction of pulp with oxygen and alkali (1-4). Many similarities to the alkali-aging reactions of cellulose exist (5,6). Although the conditions of high temperature and pressure make it difficult to demonstrate this similarity, the goal can be achieved with modified conventional equipment and appropriate experimental design.

## EXPERIMENTAL

The apparatus was designed around a 2-liter stainless steel Parr Bomb. The reaction was limited to 100°C so that steam could be used for preheating the pulp as well as for expelling air without significantly altering the pulp consistency. The reaction and the apparatus were automatically monitored with thermocouples at critical points, and pressure changes were measured with a conventional Bourdon gage and a Pace d/p Transducer. Since the pulp was reacted at 25% consistency, no mixing was possible.

The southern pine kraft pulp (22.7% GE Brightness, 20.5 permanganate no., 29.0 cps viscosity, and 15.3 km zero-span breaking length) was provided by Champion International Paper Company. The transition metal ion content of the pulp was adjusted during washing to one of 3 concentrations. Before reaction the pulp was treated to achieve the desired alkalinity, consistency and 1%  $\text{MgCO}_3$  content in the manner described by Chang (1).

The chemical nature of the lignin was altered by oxidizing the pulps containing medium levels of transition metal ion with 10%  $\text{HClO}_2$  (pulp basis) at 1% consistency for 1/2 and 5 days at room temperature. Analysis confirmed the transition metal ion content after reaction and is consistent with Swan's results (4).

Samples of the least contaminated pulp were reduced with 2%  $\text{NaBH}_4$  [to destroy all carbonyl groups (12)] or 2% alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  [to destroy quinone groups (13,14) and alter the lignin (15)]. Tests showed no appreciable loss of lignin after reduction. The experimental program summarized in Table I was designed to investigate the kinetics of oxygen consumption.

In each reaction, the empty reactor was brought to 100°C in an oil bath and the pulp, in a teflon basket, was inserted into the bomb. The system was flushed with steam to remove air and to bring the pulp to 100°C. Oxygen was added to give the desired pressure and the reactor was separated from the reference cell. The reactions were terminated at appropriate times by flushing with N<sub>2</sub> and cooling. The pulps were analyzed for yield, GE Brightness (7), permanganate no. (8), TAPPI viscosity (9), zero-span breaking length (10), tear and  $\alpha$ -cellulose content (11) and pH of the liquors. Analyses of the reacted gas indicated the presence of small quantities of CO, H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>, trace organics and isotopes of O<sub>2</sub>. The consumption of oxygen as grams per 100 grams of pulp were calculated from the changes in oxygen pressure, increases in reaction temperature, and the dimensions of the reactor.

## RESULTS

The initial rapid consumption of oxygen during these reactions was followed by a slower secondary reaction after 30 to 40 minutes. An approximate initial pseudo first-order dependence of consumption on the concentration of alkali, oxygen pressure and transition metal ion content was observed. After 40 minutes the rate of consumption was dependent only on the liquor pH. This effect of metal ion and oxygen is consistent with that found in model studies (16,17). Control experiments indicated that high yield pine soda (143 and 170 kappa) pulps under the same conditions reacted at 4 times the rate and consumed 3 times as much oxygen as this commercial kraft pulp. Thus, the behavior of the kraft pulp is not due to oxygen diffusion, penetration or transfer but represents chemical reactions. No simple kinetic interpretation of these data can be made, however.

There was no simple relationship between chemical and physical properties of the isolated pulps and reaction time. Most properties changed rapidly at first and then developed at a slower limiting rate, depending on the applied experimental conditions. The change in brightness was an exception and resembled that described by Marton (18).

The relationship of pulp property to the amount of oxygen consumed is more informative. Despite the spread of results seen in Fig. 1, the extent of bleaching is related to the grams of oxygen consumed during the reaction. The graphs differ from those plotted against time by showing an independence toward alkali concentration and oxygen pressure. The bleaching action is inhibited by the presence of transition metal ions; it is not known whether this effect is due to their participation in the oxidation reaction or if it is due simply to their color in the pulp. As would be expected, the chlorited pulps exhibited the greatest brightness levels after bleaching.

Delignification of pulp is plotted against oxygen consumption in Fig. 2. The time of reaction, alkalinity, and oxygen pressure affect the delignification by changing the amount of oxygen consumed by the pulp. Transition metal ions render the reaction between lignin and oxygen slightly less effective. The reduction of carbonyl groups in the pulp affects oxygen consumption under standard conditions but does not change the amount of oxygen necessary to remove a given quantity of lignin.

Decreasing the permanganate number from 20.5 to 18 with  $\text{HClO}_2$  had a profound effect on the removal of lignin with oxygen. Although the relationship between permanganate consumption and lignin content after partial chloriting is not known, it is likely to be quite similar to the kraft relationship at low levels of oxidation. Thus it can be speculated that partial oxidation with

chlorite renders lignin more easily removed by oxygen possibly through the introduction of additional reactive phenolic groups. Other experiments with peracetic acid and peroxide confirm the profound effect of low levels of preoxidation on lignin reactivity to oxygen.

Straightforward relationships are not seen when one examines the relationship of chemical and physical properties of pulps to oxygen consumption. Pulp properties such as  $\alpha$ -cellulose content and tear (but not viscosity) resemble zero-span breaking length in its relationship to oxygen consumption. Figure 3 shows that after an initial phase of rapid degradation in which a relatively small quantity of oxygen is consumed, the reduction of strength becomes linearly related to the consumption of oxygen. At low levels of transition metal ion content, the degradation per unit oxygen consumed is not altered by changes of alkalinity, oxygen pressure or pulp reduction. When the transition metal ion content becomes large enough to overcome the beneficial effect of the added magnesium ion, the initial degradation of the pulp is accelerated by the alkalinity of the bleach. At intermediate levels of transition metal ion content, the effect of a given alkalinity is intermediate between its effect at the two extremes of contamination. It can be speculated that the rapid degradation of pulp is due to the catalytic decomposition of peroxides to harmful radical oxidants by transition metal ions. After an interval, a slower reaction sets in due to the depletion of alkali (necessary for peroxide production) and the establishment of chemical equilibria (16,17).

Oxidation of the lignin with  $\text{HClO}_2$  before oxygen bleaching did not directly alter the effectiveness of oxygen to degrade the fiber. The level of oxygen degradation is controlled by the alkalinity, the transition metal ion content of the pulp, and the amount of oxygen consumed and it is at the same level as the unmodified pulp. Pretreatment of lignin before bleaching can, therefore,

retain physical properties since less oxygen will be needed to remove equivalent amounts of lignin.

Although the relationship of oxygen consumption to pulp viscosity gave plots difficult to interpret, plots using pulp fluidity gave reciprocal results to those described in Fig. 3. The results in Fig. 4 show that at low transition metal ion contents, where the effect of magnesium ion is at a maximum, a linear relationship exists between the change in fluidity and oxygen consumption; time of reaction, oxygen pressure, alkalinity and pulp reduction do not alter the effect of oxygen on the reaction. In the presence of higher concentration of transition metal ion, the effect of these parameters is identical to those described in Fig. 3. Although pretreatments before oxygen bleaching may alter the amount of oxygen consumed, it does not alter the predominating action of alkalinity and transition metal ion on pulp degradation.

The data indicate that the reactions of lignin and carbohydrate have different mechanisms. It is possible that these reactions of both carbohydrate and lignin that lead to oxygen consumption and peroxide formation will also result in additional cellulose or pulp degradation. The effect of lignin on cellulose degradation has already been demonstrated (5,6) but can be reduced if the harmful degradation products can be minimized by destroying peroxide precursors within the pulp or by introducing functional groups which, although they are peroxide precursors, facilitate lignin removal.

This similarity between fiber degradation and cellulose degradation suggests that an empirically simple relationship exists between them. Although the plot shown in Fig. 5 tends to confirm this conjecture, the deviations from linearity suggest other factors also play an important role. The approximately



linear relationship suggests that the increase in the number of cellulose molecules caused by chain cleavage is related to fiber strength. A similar relationship has been shown by Flory (19) and others (20) to occur between fluidity and the strength of films and filaments, formed from cellulose derivatives and other polymers.

This relationship is probably not the only one involved here since the true fluidity of a polymer is related to the inverse of the number average molecular weight, whereas the "fluidities" employed here are inversely related to a predominantly weight average approximation of molecular weight. In addition a fiber network cannot be expected to respond to stresses in the same manner as single filaments and films — especially since the zero-span jaws have a finite span of about 300  $\mu\text{m}$ . Interfiber effects are, therefore, to be anticipated. These complications may be illustrated by the observations of Swenson (21) that oxygen bleached pulps (prepared at The Institute of Paper Chemistry) having a much more limited range of viscosity and zero-span than those studied here, showed a closer relationship to the weight average molecular weight than to the number average molecular weight or its reciprocal.

Such contradictory results may be rationalized on the basis of different pulp compositions. The pulps studied by Swenson contained negligible quantities of transition metal ion whereas all the pulps studied here contained significant quantities of these ions. The nature and location of these components in the cell wall might affect oxidation; in other instances the nature and location of preliminary fiber damage might direct chemical degradation to particular locations on the fiber.

## SUMMARY AND CONCLUSIONS

In the case of pulps relatively free of transition metal ion and stabilized with magnesium ion, the removal of lignin is related to the consumption of oxygen. Factors such as alkalinity and oxygen pressure speed up the process but do not alter this relationship appreciably. The degradation of the fiber is almost linearly related to the consumption of oxygen and is not altered by variations in alkalinity, reduction of lignin and oxygen pressure.

In the presence of transition metal ion, the removal of lignin by oxygen is less efficient, whereas the degradation of the fiber is initially greatly increased with increases of alkalinity and transition metal ion content. Ultimately a steady state of degradation is achieved which seems common to all experimental conditions.

The complementary behavior of changes in zero-span and fluidity leads to an approximately linear relationship between them. The chemical and physical significance of the observation is masked by experimental and theoretical uncertainties.

The results indicate that lignin and carbohydrate react with oxygen by different mechanisms. They also suggest, in agreement with the speculations of Akim (22), that the products of these reactions — various peroxides — degrade the carbohydrate components through the catalytic action of alkali and transition metal ion. The initial increased efficiency of fiber degradation by oxygen suggests the occurrence of a degradative chain reaction. The results suggest that the delignification of lignin-rich pulps would be accompanied by a corresponding increase in cellulose degradation.

The effect of this catalytic activity can be modified by minimizing peroxide precursors in the pulp and by rendering the lignin more soluble during the bleaching reaction. Although these manipulations do not alter the basic relationships between the quantity of oxygen consumed, the alkalinity and the transition metal ion content, they do minimize exposure of the fiber to the harmful intermediates.

#### LITERATURE CITED

1. Chang, H. M. and Kleppe, P. J., Tappi 56:97(1973); Chang, H. M. and Eckert, R. C., Pulp Paper Mag. Can. 73(12):T-400(1972).
2. Husvrita, L., Paperi Puu 52(7):439(1970).
3. Eachus, S. W., TAPPI Ann. Mtg. (NY) Preprint, Feb. 24-26, 1975:167.
4. Gustavsson, R. and Swan, B., Tappi 58(3):120(1975).
5. Samuelson, O. and Stolpe, L., Svensk Papperstid. 72(20):662(1969); 74(18):545(1971); Papier 24:671 (1970).
6. Ericsson, B., "Oxygen Oxidation of Cellulose in Aqueous Alkaline Medium," Ph.D. thesis, Stockholm, 1974.
7. TAPPI T 217 m-48.
8. TAPPI T 214 m-50.
9. TAPPI T 230 sm-50.
10. TAPPI T 231 sm-50.
11. TAPPI T 203 m-58.
12. Aspinall, G. O. and Tan, S. C., Carbohydr. Res. 38:71(1974).
13. Pal'mova, S. B. and Bogomolov, B. D., Izv. Vyssh. Ucheb. Zaved., Les. Zh. 12(4):102(1969).
14. Morello, J. A., Craw, M. R., Constantine, H. P., and Foster, R. E., J. Appl. Physiol. 19:522(1964).
15. Roymoulik, S. K., U.S. patent 3,716,448(Feb. 13, 1973).

16. Sinkey, J. D. and Thompson, N. S., Paperi Puu 56(3):473(1974); McCloskey, J. T., Sinkey, J. D., and Thompson, N. S., Tappi 58(2):56(1975); McCloskey, J. T., Sinkey, J. D., Thompson, N. S., and Schroeder, L. R., Paperi Puu 57(3):131(1975).
17. Brooks, R. D. and Thompson, N. S., Tappi 49(8):362(1966).
18. Marton, R., Leopold, B., Kartovaara, I., and Koeppicus, R., Can. Wood Chem. Symp. Extended Abstract Papers, Presentation 4:45 (July 4-6, 1973).
19. Flory, P. J., J.A.C.S. 67(12):2048(1945).
20. Wakeham, H., "Mechanical Properties of Cellulose and its Derivatives," In Ott and Grafflin's "Cellulose and Cellulose Derivatives," Part III, Interscience, New York, 1955, Chap. XI.
21. Swenson, H. A., Svensk Papperstid. 78(2):61(1975).
22. Akim, G. L., Sul'fat. Varka Otbelka Polufab. Kislородom, Kiev 1972:30-50; ABIPC 44:1501(1973).

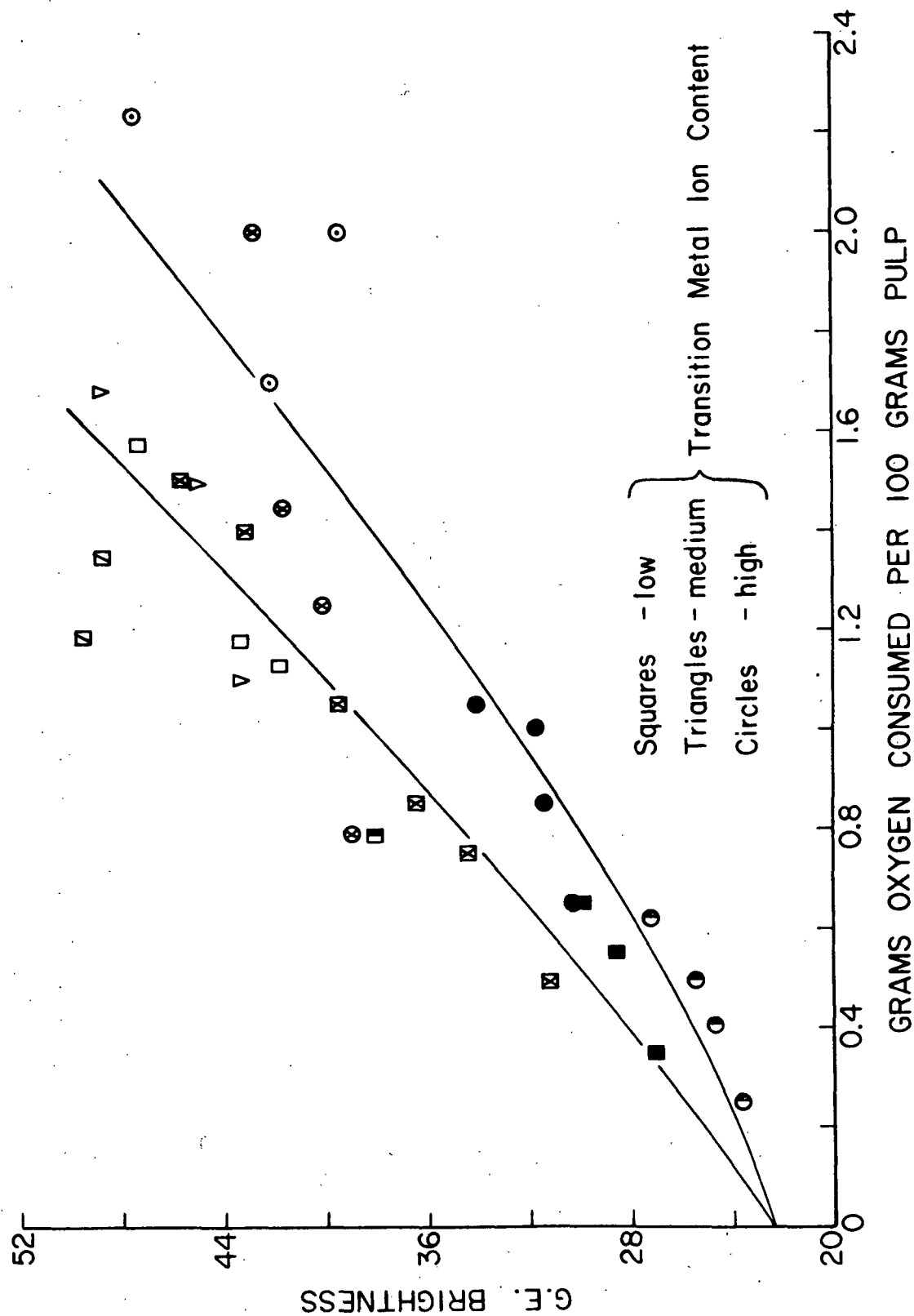


Fig. 1. The relationship between grams of oxygen consumed and GE brightness attained after bleaching southern pine kraft pulp at 100°C, 25% consistency in the presence of 1%  $MgCO_3$ .\*

\*See Table I for the significance of the symbols used in plots.

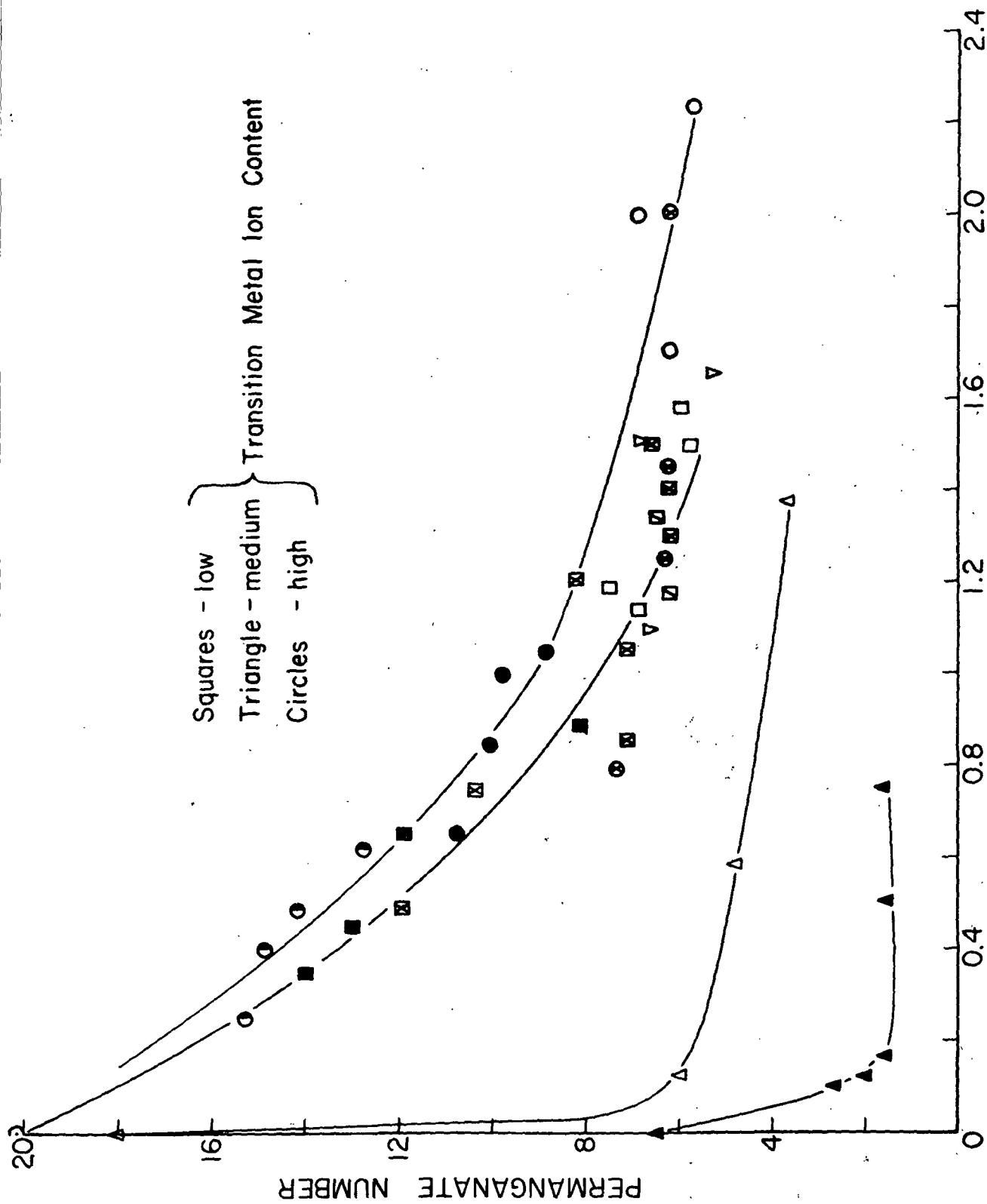


Fig. 2. The relationship between grams of oxygen consumed and permanganate number after bleaching southern pine kraft pulps at 100°C, 25% consistency in the presence of 1%  $MgCO_3$ .\*

\*See Table I for the significance of the symbols used in plots.

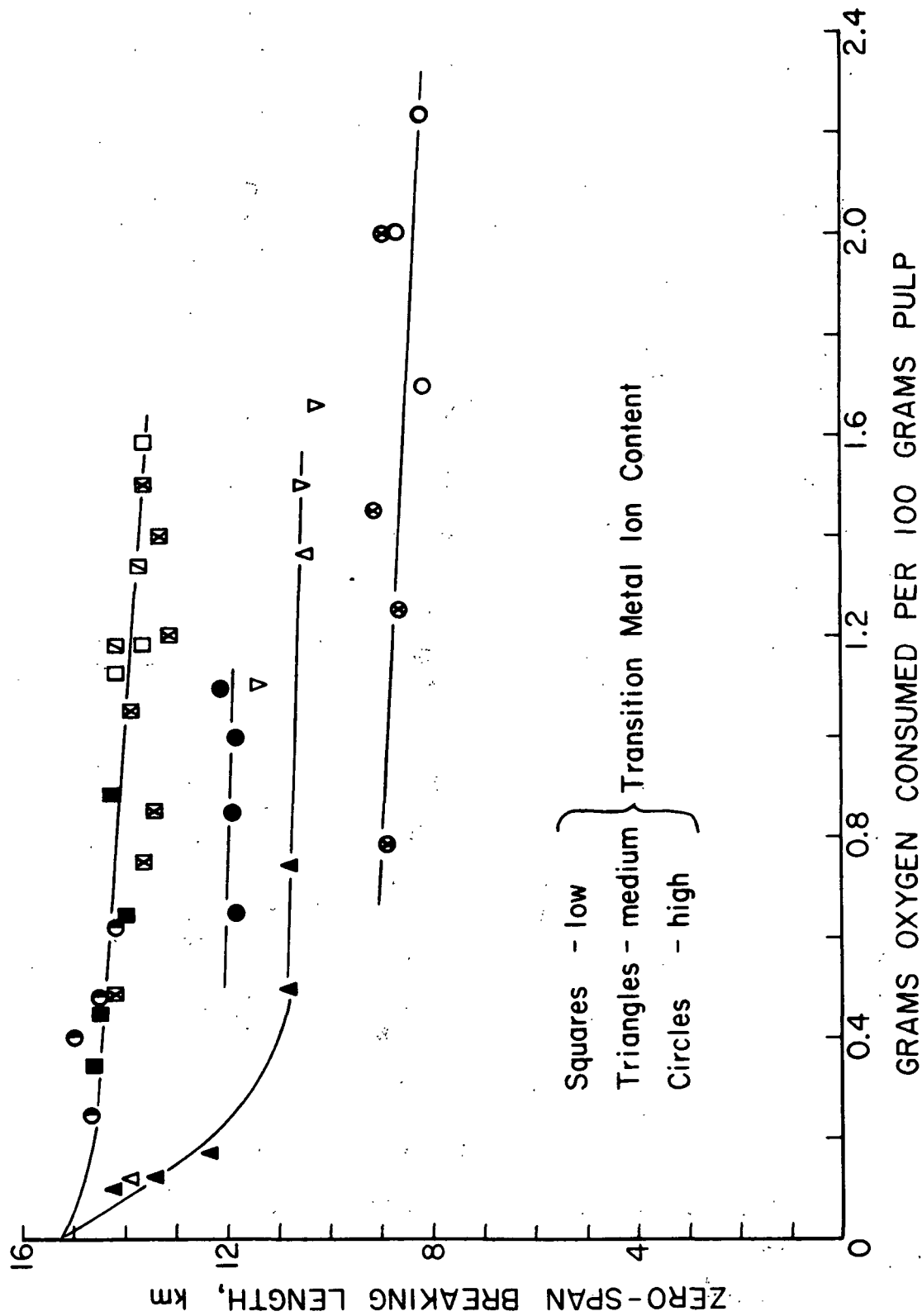


Fig. 3. The relationship between grams of oxygen consumed and zero-span breaking length after bleaching southern pine kraft pulp at 100°C, 25% consistency in the presence of 1%  $\text{MgCO}_3$ .\*

\*See Table I for the significance of the symbols used in plots.

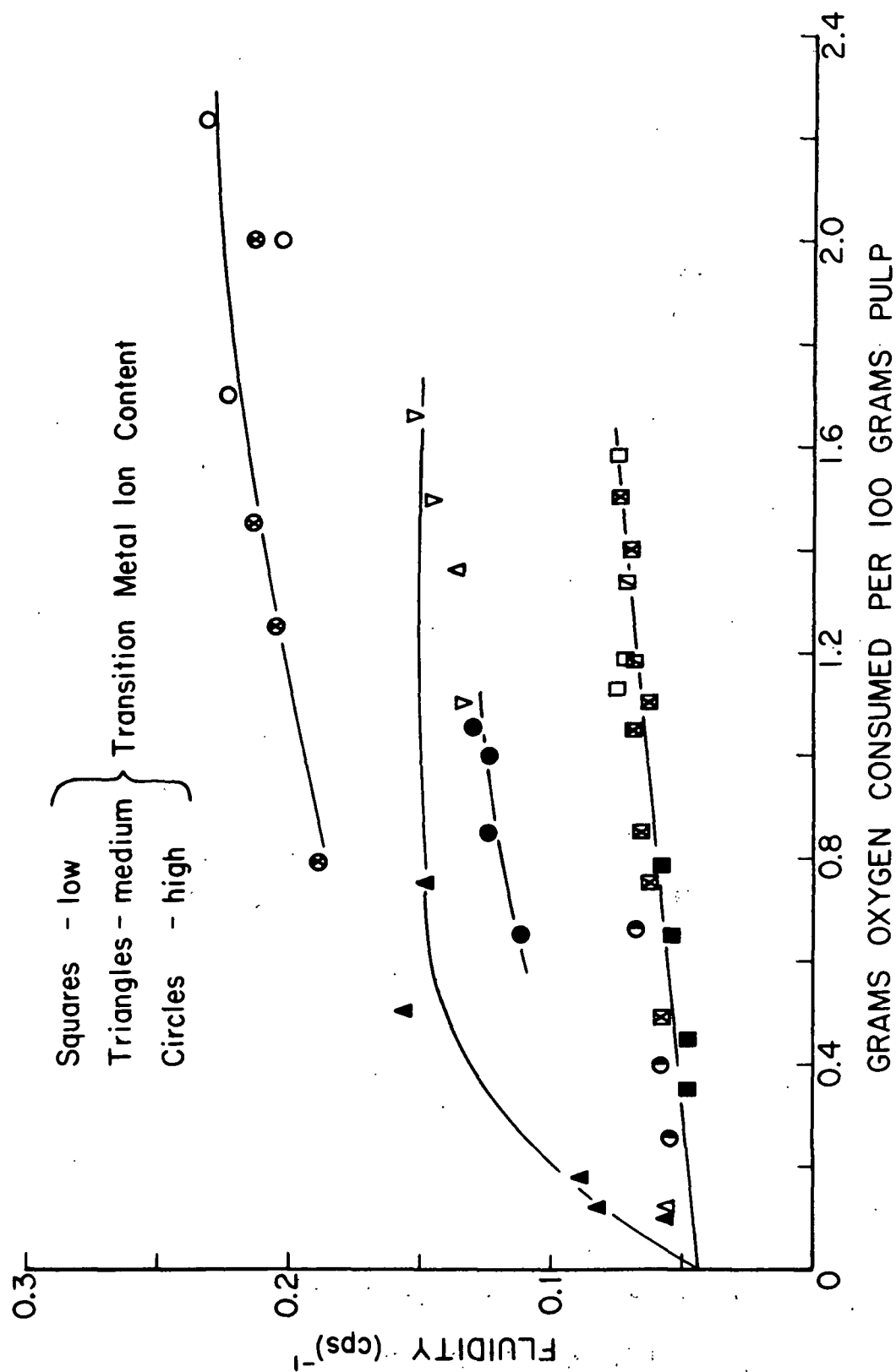


Fig. 4. The relationship between grams of oxygen consumed and fluidity (cps)<sup>-1</sup> after bleaching southern pine kraft pulps at 100°C, 25% consistency in the presence of 1% MgCO<sub>3</sub>.\*

\*See Table I for the significance of the symbols used in plots.



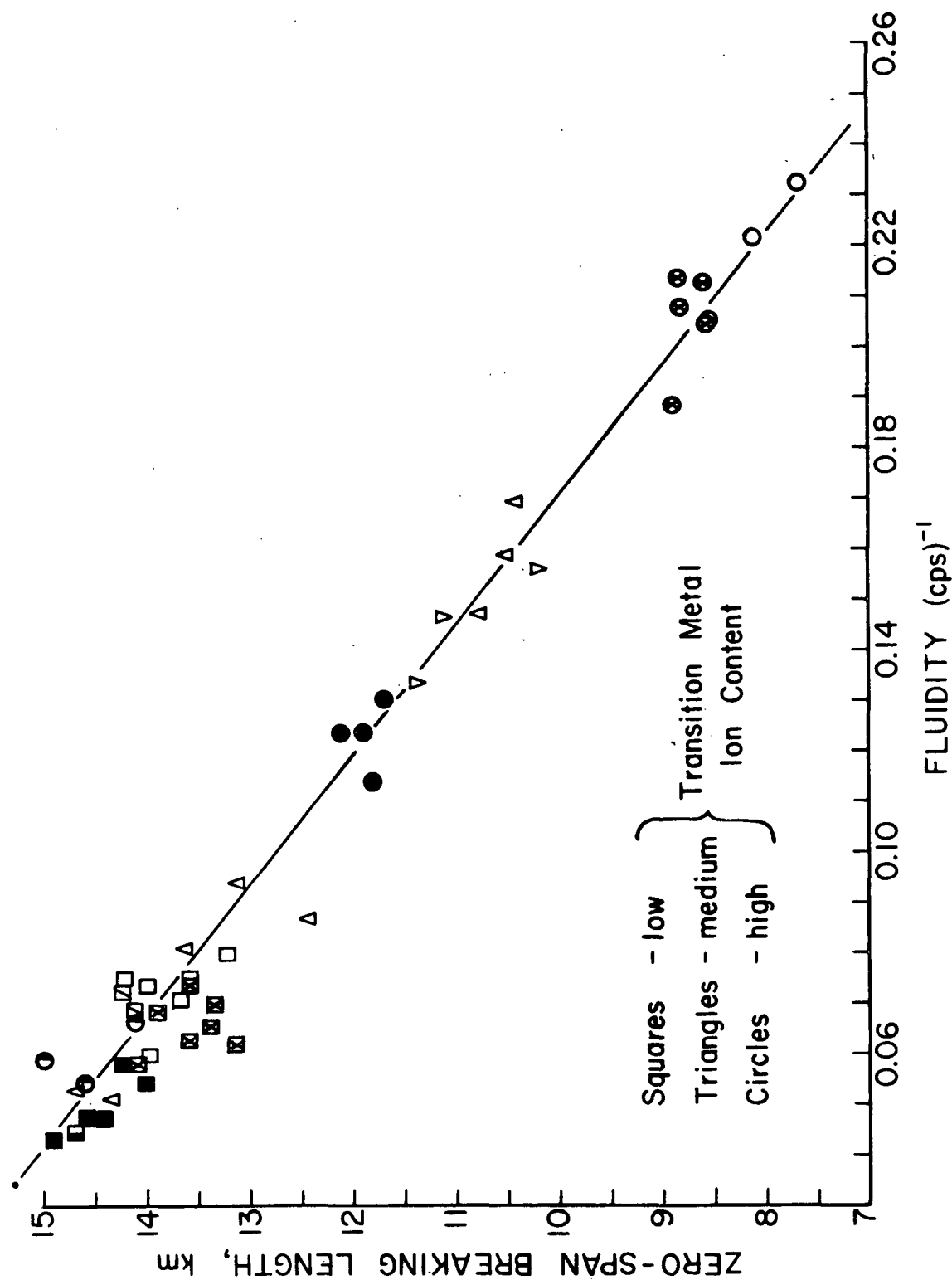














Fig. 5. The relationship between zero-span breaking length and fluidity  $(\text{cps})^{-1}$  for southern pine kraft pulps bleached with oxygen under a variety of conditions.\*

\*See Table I for the significance of the symbols used in plots.

Table I. Experimental Design and Symbols Used in Plotting Results of Pine Pulp Oxidation

Transition metal ion content	Low, 74 ppm	Medium, 121 ppm	High, 246 ppm
6.6% Alkalinity	 <sup>a</sup>	 <sup>b</sup>	 <sup>b</sup>
3.3% Alkalinity	 <sup>a</sup>		 <sup>b</sup>
1.7% Alkalinity	 <sup>a</sup>		 <sup>b</sup>
Pressure variations <sup>c</sup>			
Partially oxidized <sup>d</sup>			
18 K. No.			
1.6 K. No.			
Partly reduced <sup>e</sup>			

<sup>a</sup>Reactions at 130 psig O<sub>2</sub> stopped at 5, 10, 15, 30, 60, and 120 minutes.

<sup>b</sup>Reactions at 130 psig O<sub>2</sub> stopped at 15, 30, 60, and 120 minutes.

<sup>c</sup>Conducted at 65, 97.5, and 195 psig O<sub>2</sub>, 6.6% alkalinity, for 120 minutes.

<sup>d</sup>Conducted at 1.7, 3.3, and 6.6% alkalinity, 130 psig O<sub>2</sub>.

<sup>e</sup>Reduced with alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> or NaBH<sub>4</sub>; 6.6% alkali, 130 psig O<sub>2</sub>, 120 minutes.